



Zinc barrel electroplating using low cyanide electrolytes

M. WERY^{1*}, J.C. CATONNÉ², V. LIGIER¹ and J. PAGETTI¹

¹Laboratoire de Corrosion et de Traitements de Surface, Université de Franche-Comté, 32, Rue Mégevand, 25030 Besançon Cedex, France;

²Laboratoire d'Electrochimie Industrielle, Conservatoire National des Arts et Métiers, Paris, France

(*author for correspondence, e-mail: martine.wery@univ-fcomte.fr; fax: +33 381 666858)

Received 4 June 1998; accepted in revised form 5 October 1998

Key words: cathode efficiency, deposit morphology, electrolyte composition, factorial fractional design, zinc electrodeposition

Abstract

The influence of plating conditions on the cathode efficiency of zinc barrel electroplating and the quality of deposited layers for low cyanide electrolytes is analysed. The investigations are carried out using factorial design methodology. The first part of the study shows how electrolyte components, such as brightening agent, sodium carbonate concentration, sodium hydroxide concentration, sodium cyanide concentration and zinc metal content, influence cathode efficiency and the morphology and the texture of the zinc electrodeposits. A mathematical model that fits experimental data is suggested and the pseudo three-dimensional plot of yield as a function of electrolyte composition for three significant component mixtures, brightening agent, sodium cyanide concentration and zinc metal content, is represented. The second part of the study shows how varying six process parameters influences current efficiency and metal thickness distribution. For the range studied, efficiency is affected by workload volume, current density, perforation and part size, but not by rotation speed and quantity of charge.

1. Introduction

Zinc electroplating is extensively used in the fasteners when components are subject to the risk of atmospheric corrosion. In these applications, it is necessary to electroplate thick layers of zinc, typically 10 µm, and this is achieved with acid as well as alkaline solutions. Intricately shaped pieces are usually plated in alkaline cyanide electrolytes where cathodic polarization is higher and more uniform thickness is obtained. Plating techniques are commonly subdivided into rack, barrel and 'high rate' plating [1]. Barrel plating has long been used for mass producing large numbers of small parts because it is cheaper and more convenient than racking procedures [2]. The nonconducting barrel, usually plastic, is round or hexagonal with holes drilled in it. It is partially or fully immersed in a vat containing anodes on two sides of the tank (Figure 1) and rotated horizontally. The workload, consisting of identical small parts to be plated, can be considered to be a porous electrode. The workload is tumbled inside the barrel, permeated

and covered by the electrolyte to expose the parts to plating conditions. Current is often fed to the workload through a flexible dangle contact that is dynamic relative to the parts. Barrel plating conditions are different from other plating processes because of the shape of the cathode (porous electrode), current fluctuations corresponding to the intermittent contact of tumbling parts with the electrical lead and mass transfer exchange.

To plate parts correctly, it is important to determine the factors that affect cathodic efficiency, including the properties of zinc deposits and methods needed to optimize processing. Over the last three or four decades, many theories have been advanced as to what takes place in the plating barrel [3–7]. Statistical studies have been carried out to determine not only the factors affecting metal distribution [8–11] but also the optimum conditions required for barrel plating [11–14]. However, a review of the literature reveals little information on the factors that influence cathodic efficiency during barrel plating [9, 11, 12]. Although cathodic efficiency is

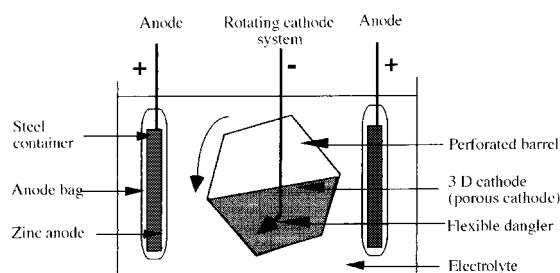


Fig. 1. Schematic cross section of zinc plating reactor.

important for all types of metal plating, it is even more important in zinc plating because commercial zinc electroplating in barrels is widespread and because of the endemic problem of hydrogen embrittlement of steel parts [13, 15–17].

Plating factors are generally divided into three categories: (i) *equipment factors*, including the type of barrel, size of holes, rotation speed, load size, (ii) *plating condition factors*, such as apparent current density, electrolysis time, thickness of the deposit, and hydrodynamic conditions, (iii) *electrolyte composition factors*.

Most of the previous studies on barrel plating investigated each parameter one at a time while keeping the others constant. We have viewed the problem from a different angle. Because parameters in a plating operation are numerous and coexist in complex relationships, the factorial design seems the most suitable experimental approach for studying zinc barrel plating. It is impossible to study all the numerous variables at once. Therefore, this study was divided into two parts. In the first part, we determined the effects of solution factors only, including the influence of the components of a low cyanide zinc electrolyte on cathodic efficiency and the morphology of electrodeposits. In the second part, cathodic efficiency and metal thickness distribution as a function of equipment and plating conditions were studied.

2. Experimental details

2.1. Plating facilities

The experimental study was carried out on a laboratory scale with an electrolytic cell that is a reproduction of an industrial one (1/1000). The dimension for the pilot plant is based on a constant ratio of the number of amperes per volume and charge per surface. To reduce the number of variables, plating was performed using the same type of barrel, cathode substrate, anode

geometry and plating preparation procedure. A small horizontal-type cylindrical barrel, with integral-mesh moulded baskets (effective capacity of 0.282 L, 0.03 or 0.5 mm² perforations) was used. The barrel was equipped with a flexible dangle contact to carry the current to the plating arrangement. The barrel was fully immersed in a cell containing 1.5 L plating solution at a temperature thermostatically controlled within 1 °C and stirred with a pump. The rotational speed of the barrel was adjustable. A precalibrated, digital coulombmeter was connected in series with the barrel to measure the coulombs passed during each plating period.

All samples were pretreated before electroplating by soaking them in an alkaline solution to remove phosphate films and grease, then by cleaning them electrolytically and finally by dipping them in an acid. Parts were then rinsed, dried and carefully weighed. At the end of the plating cycle, the weight gain of parts was determined. Cathodic efficiency was calculated by comparing actual weight gain with that predicted from a knowledge of the total coulomb charge passed. In all cases, duplicate tests were run.

The anodic system was composed of high-grade zinc anodes in steel containers, fitted in anode bags to prevent the fine particles formed at the anode from migrating to the cathode and thus increasing plating roughness. A preliminary study was made to determine the anode area (steel to zinc anode ratio) needed to maintain a stable zinc concentration in the system. Solutions were analysed before and after electrolysis. In all cases, the change in electrolyte composition was found to be insignificant.

Low cyanide concentration plating solutions were prepared with commercial grade chemical products (ZnO, NaOH and NaCN) and an organic brightener supplied by the Continentale Parker Company.

In the first part of the study (influence of electrolyte components), small steel rivets (grade XC38) were selected as test parts. A load of two hundred rivets ($S = 4.8 \text{ dm}^2$) was used since this is an optimum number for obtaining uniform thickness during barrel plating. The current density was 10 mA cm^{-2} . The plating time was 42 min for each test (for a theoretical thickness of $12 \text{ }\mu\text{m}$).

Two batches of thin-wire, carbon-steel cotter pins, having the same specifications apart from size ($S_{\text{pin1}} = 0.92 \text{ cm}^2$, $S_{\text{pin2}} = 3.57 \text{ cm}^2$), were used in the second part of the study.

2.2. Characterization of deposits

Deposits were examined by scanning electron microscopy (Cambridge Stereoscan 120 microscope) to deter-

mine surface morphology and by X-ray diffraction (Philips X-pert MPD) to determine their preferred orientation relative to the ASTM standard for zinc powder.

To determine some of the physical factors that influence zinc metal distribution in barrel loads, the variation coefficient V , percentage of standard deviation from the mean, was determined as

$$V = \sqrt{\frac{(\bar{d} - d_1)^2 + \dots + (\bar{d} - d_n)^2}{n - 1}} \times \frac{100}{\bar{d}}$$

with d_i the individual coating thickness, n the number of measurements and \bar{d} the average coating thickness. The procedure involved sampling 30 parts from the barrel load, using a Fisherscope 1600 X-ray fluorescence apparatus.

3. Results and discussion

3.1. Influence of the electrolyte composition on cathodic efficiency η and on morphology of deposits

3.1.1. Cathode efficiency

The constituents of the low cyanide electrolyte that have the greatest and least influence on cathode efficiency, η , over the ranges studied are identified. The nature of plating experiments lends itself to an experimental design. A fractional factorial design called 2^{5-1} , using fewer runs than a full design, and involving five factors with each factor at two levels [18, 19], is chosen. That design comprises 16 experiments (Table 1) and is constructed by setting **5 = 1234**. The notation for the

mathematical treatment uses respectively, a ‘−1’ and a ‘+1’ to indicate the low level and high level of the variable. Table 2 depicts the five factors studied which are brightening agent (A), sodium carbonate concentration (C), sodium hydroxide concentration (H), sodium cyanide concentration (N) and zinc metal content (Z), and their settings in the factorial test matrix. Several authors have described the test program in detail [18, 19]. Experiments are carried out in a random order to avoid uncontrolled effects on results.

Effects on results are normalized and given as percentage change in the test results when going from the defined lower level to the defined higher level factor. The Yates algorithm was used to estimate the factorial effects and construct the associated analysis of variance (ANOVA) table.

Table 3 gives the results of the factorial analysis. Comparing the estimates suggests that sodium carbonate (C) and caustic soda (H) are not significant factors for the range studied. Therefore, it is difficult to establish their accurate functions. We focused on those effects that are reasonably large in magnitude, including the main effects of a brightening agent ($A = -12.9$), sodium cyanide concentration ($N = -3.0$) and zinc metal content ($Z = 4.8$), but also appreciate interactions ($AZ = 4.4$) and ($AN = -2, 4$). Therefore, the response η can be represented by a first order model, that fits the data [18]:

$$\eta = 82.3 - 12.9 \times A - 3.0 \times N + 4.8 \times Z + 4.4 \times AZ - 2.4 \times AN$$

An additional ‘center point’ experiment was run to validate this model. The comparison between the experimental response (82.2) and the theoretical one

Table 1. Factorial experimental design 2^{5-1} with the generator **I = 12345**

Test	1+ 2345	2+ 1345	12+ 345	3+ 1245	13+ 145	23+ 145	45+ 123	4+ 1235	14+ 235	24+ 135	35+ 124	34+ 125	25+ 134	15+ 234	5+ 1234	I+ 12345
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	1
3	1	1	1	−1	−1	−1	−1	1	1	1	1	−1	−1	−1	−1	1
4	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	1	1	1	1	1
5	1	−1	−1	1	1	−1	−1	1	1	−1	−1	1	1	−1	−1	1
6	1	−1	−1	1	1	−1	−1	−1	−1	1	1	−1	−1	1	1	1
7	1	−1	−1	−1	−1	1	1	1	1	−1	−1	−1	−1	1	1	1
8	1	−1	−1	−1	−1	1	1	−1	−1	1	1	1	1	−1	−1	1
9	−1	1	−1	1	−1	1	−1	1	−1	−1	−1	1	−1	1	−1	1
10	−1	1	−1	1	−1	1	−1	−1	1	1	1	−1	1	−1	1	1
11	−1	1	−1	−1	1	−1	1	1	−1	−1	−1	−1	1	−1	1	1
12	−1	1	−1	−1	1	−1	1	−1	1	1	1	1	−1	1	−1	1
13	−1	−1	1	1	−1	−1	1	1	−1	1	1	1	−1	−1	1	1
14	−1	−1	1	1	−1	−1	1	−1	1	−1	−1	−1	1	1	−1	1
15	−1	−1	1	−1	1	1	−1	1	−1	1	1	−1	1	1	−1	1
16	−1	−1	1	−1	1	1	−1	−1	1	−1	−1	1	−1	−1	1	1

Table 2. Levels for the electrolyte parameters

	Factor 1 B Brightening agent content /ml L ⁻¹	Factor 2 C Sodium carbonate concentration /mol L ⁻¹	Factor 3 H Sodium hydroxide concentration /mol L ⁻¹	Factor 4 N Sodium cyanide concentration /mol L ⁻¹	Factor 5 Z Zinc concentration /mol L ⁻¹
Low level -1	0.0	0.00	1.88	0.41	0.15
Central level	1.0	0.28	2.00	0.51	0.19
High level +1	2.0	0.57	2.12	0.61	0.23

Table 3. Results and effects of the constituents of the low cyanide electrolyte upon the cathodic efficiency η

Test	η_1 /%	η_2 /%	η_{average} /%	Response notation		Effects	Significant*
1	77.4	77.1	77.3	Mean ₊₊₊	I ₊₊₊	82.3	
2	67.2	66.7	67.0	B ₊₊₊	1 ₊₊₊	-12.9	yes
3	50.7	50.3	50.5	C ₊₊₊	2 ₊₊₊	0.2	no
4	83.6	83.1	83.4	H ₊₊₊	3 ₊₊₊	0.9	no
5	56.9	56.5	56.7	N ₊₊₊	4 ₊₊₊	-3.0	yes
6	82.4	82.1	82.3	Z ₊₊₊	5 ₊₊₊	4.8	yes
7	71.7	71.1	71.4	B C ₊₊₊	12 ₊₊₊	-0.1	no
8	66.4	66.2	66.3	B H ₊₊₊	13 ₊₊₊	0.6	no
9	94.7	94.3	94.5	B N ₊₊₊	14 ₊₊₊	-2.4	yes
10	95.9	96.2	96.1	B Z ₊₊₊	15 ₊₊₊	4.4	yes
11	95.5	95.8	95.7	C H ₊₊₊	23 ₊₊₊	0.3	no
12	95.8	95.7	95.8	C N ₊₊₊	24 ₊₊₊	-0.1	no
13	95.5	95.7	95.6	C Z ₊₊₊	25 ₊₊₊	0.7	no
14	95.6	95.9	95.8	H N ₊₊₊	34 ₊₊₊	0.8	no
15	93.1	92.7	92.9	H Z ₊₊₊	35 ₊₊₊	-0.2	no
16	95.7	95.0	95.4	N Z ₊₊₊	45 ₊₊₊	0.8	no

* After analysis of variables (ANOVA)

(82.3, calculated from the first order polynomial) confirms that the response η is a first order function of the three factors.

The results require interpretation. An additive in the electrolyte should change the mechanism of the cathode process. Its action, connected to the variation in the partial coverage for H_{ads} and Zn_{ads}^I , increases the cathodic overvoltage and favours hydrogen discharge at the electrode. The additive therefore diminishes current efficiency. The effects of sodium cyanide (N) and zinc (Z) which, respectively, show a negative and a positive slope, are akin to thermodynamic considerations and indicate the importance of local pH near the cathode [20]. It is well established that changes in cathodic efficiency are primarily affected by the interrelation of cathode reactions, metal deposition, and hydrogen evolution. The local pH increase resulting from solvent reduction, modifies the equilibrium. Results confirm observations of other investigators [21, 22] that it is necessary to maintain an adequate $[Zn]/[NaCN]$ ratio.

Within what limits then must the constituents be controlled to maintain maximum efficiency? Contour plots are helpful in answering this question (Figure 2). They show what may happen if variables are changed together, and deal with the optimization of system performance. To optimize cathodic efficiency, it is suggested that the cyanide and brightener agent are set to a lower level and the zinc metal to a higher level. However, adding no brightener alters the appearance of the metal deposit. A compromise must be reached because zinc coatings must resist corrosion and have adequate decorative properties, even if the vast majority of these types of parts are functional.

3.1.2. Morphology of deposits

The effect of the electrolyte composition is characterized by studying the deposit morphology using plating solutions of various compositions. Three aspects have been identified (Figure 3): (i) zinc platelets, (ii) entangled needles, (iii) uniform and bright fine grain film obtained for zinc electrodeposits prepared in an electrolyte with

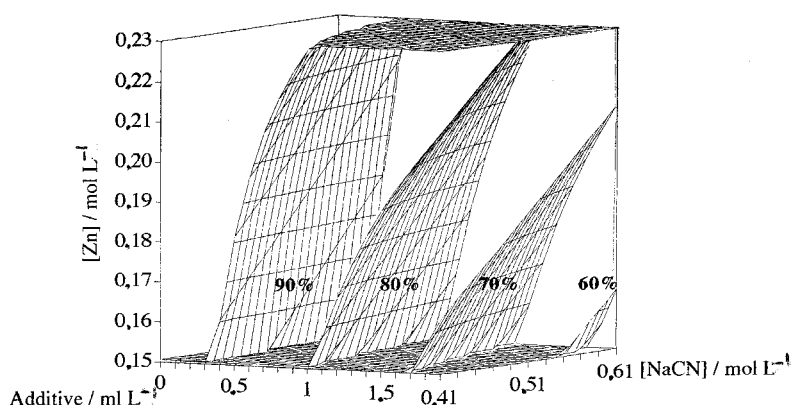


Fig. 2. Pseudo three-dimensional plot of response (cathode efficiency) as a function of composition for a three-component low cyanide zinc plating electrolyte.

an additive. Figure 4 compares the crystal morphology of coatings produced from solutions without an additive. The high cyanide content changes a coarse-grained deposit into a fine-grained surface (micrographs 4(c) and (g)). Cyanide content seems to affect the growth rate resulting in a limitation of the average size of germs during coalescence periods. These deposits are characterized by pronounced $(11\bar{2}0)(21\bar{3}1)$ preferred orientations. The changes in morphology and orientation may be directly related to the $[Zn]/[NaCN]$ ratio. Even if sodium carbonate does not significantly influence the morphology for the range studied, it seems to increase the $(11\bar{2}0)$ texture. For all morphologies studied, we observed a crushing of crystallites due to a mechanical effect that is specific to the plating technologies studied.

Adding small amounts of brighteners to the electrolyte beneficially affects zinc morphology. Grain refinement is improved due to the high nucleation density. Moreover, adding brighteners considerably modifies the polarisability of the electrochemical system as more hydrogen evolves. The surface has a mirror appearance and only some holes, $0.1\ \mu\text{m}$ in diameter, which demonstrates the presence of evolved hydrogen (Figure 3(c)). The brightener molecule, composed of nitrogen atoms, is probably cationic, considering the alkaline character of the electrolyte. It adsorbs onto anionic sites, since the electrolyte's pH is greater than the isoelectric point of zinc (~ 9.2) because the zinc surface has an excess of negative charges. The growth of the crystals therefore is inhibited, bidimensional nucleation reduces grain size, and the $(10\bar{1}0)$ orientation is favoured. It is possible to incorporate the brightener into the deposit. To verify this, the surface of zinc deposits prepared from four electrolytes without any additive or with 1, 2 and $5\ \text{ml L}^{-1}$ of brightening agent (Figure 5), were analysed using 'glow discharge optical spectrometry'. The con-

centration profiles of elements such as carbon, nitrogen, zinc and copper, are determined. For these surface analyses, zinc is deposited onto a copper substrate to avoid the influence of the steel substrate, the source of carbon. No carbon trace is recorded for the copper substrate, but a background noise of nitrogen is revealed and corrected. Figure 6 shows that both C and N tracers are incorporated into the zinc deposit. Their quantities are proportional to the bulk concentration of additives, which are incorporated as the plating layer forms.

3.2. Experiment design for equipment and plating condition factors

3.2.1. Cathode efficiency

The second part of this paper deals with cathodic efficiency and variation in deposit thickness for barrel loads as a function of equipment and type of load. Previous investigations have indicated that equipment factors are as important, and in some cases more important, than solution and plating conditions [2, 8]. In the first part of this study, we showed that statistical methods are useful for determining which variables influence cathodic efficiency the most. Therefore, a similar approach in the second part of the study was used. Six factors were studied workload volume (V), rotation speed (R), electrical charge (Q), current density (I), perforation size (P) and part size (S). Table 4 gives their settings in the factorial test matrix. A 2^{6-2} fractional design was chosen, constructed by setting $5 = 123$ and $6 = 124$, generating relations $I = 1235 = 1246$. This configuration provides first order estimates (main effect of the variables) without the interaction of two factors. The complete defining relation for this design, obtained by taking the generators first one at a time and then by multiplying them

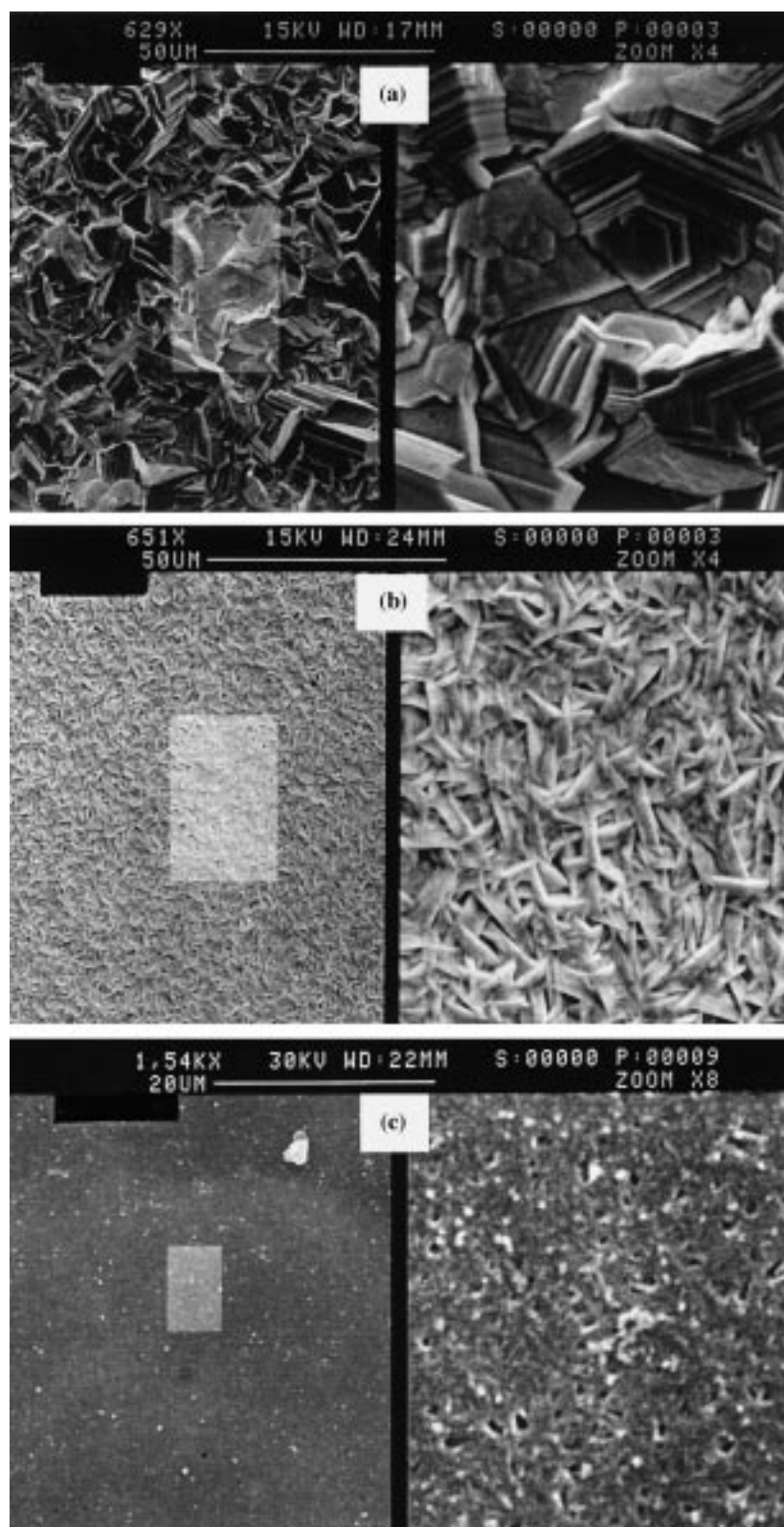


Fig. 3. SEM observations of zinc deposits – low cyanide zinc plating electrolyte: $i = 10 \text{ mA cm}^{-2}$ after electrolysis with 25.2 C cm^{-2} , (a) ($\text{Zn } 0.23 \text{ mol L}^{-1} + \text{NaOH } 2.13 \text{ mol L}^{-1} + \text{NaCN } 0.41 \text{ mol L}^{-1} + \text{Na}_2\text{CO}_3 0.57 \text{ mol L}^{-1}$), (b) ($\text{Zn } 0.16 \text{ mol L}^{-1} + \text{NaOH } 2.13 \text{ mol L}^{-1} + \text{NaCN } 0.61 \text{ mol L}^{-1}$) and (c) ($\text{Zn } 0.15 \text{ mol L}^{-1} + \text{NaOH } 2.13 \text{ mol L}^{-1} + \text{NaCN } 0.61 \text{ mol L}^{-1} + \text{commercial brightener } 1 \text{ ml L}^{-1}$). Scalebars: (a) 50 μm ; (b) 50 μm ; (c) 20 μm .

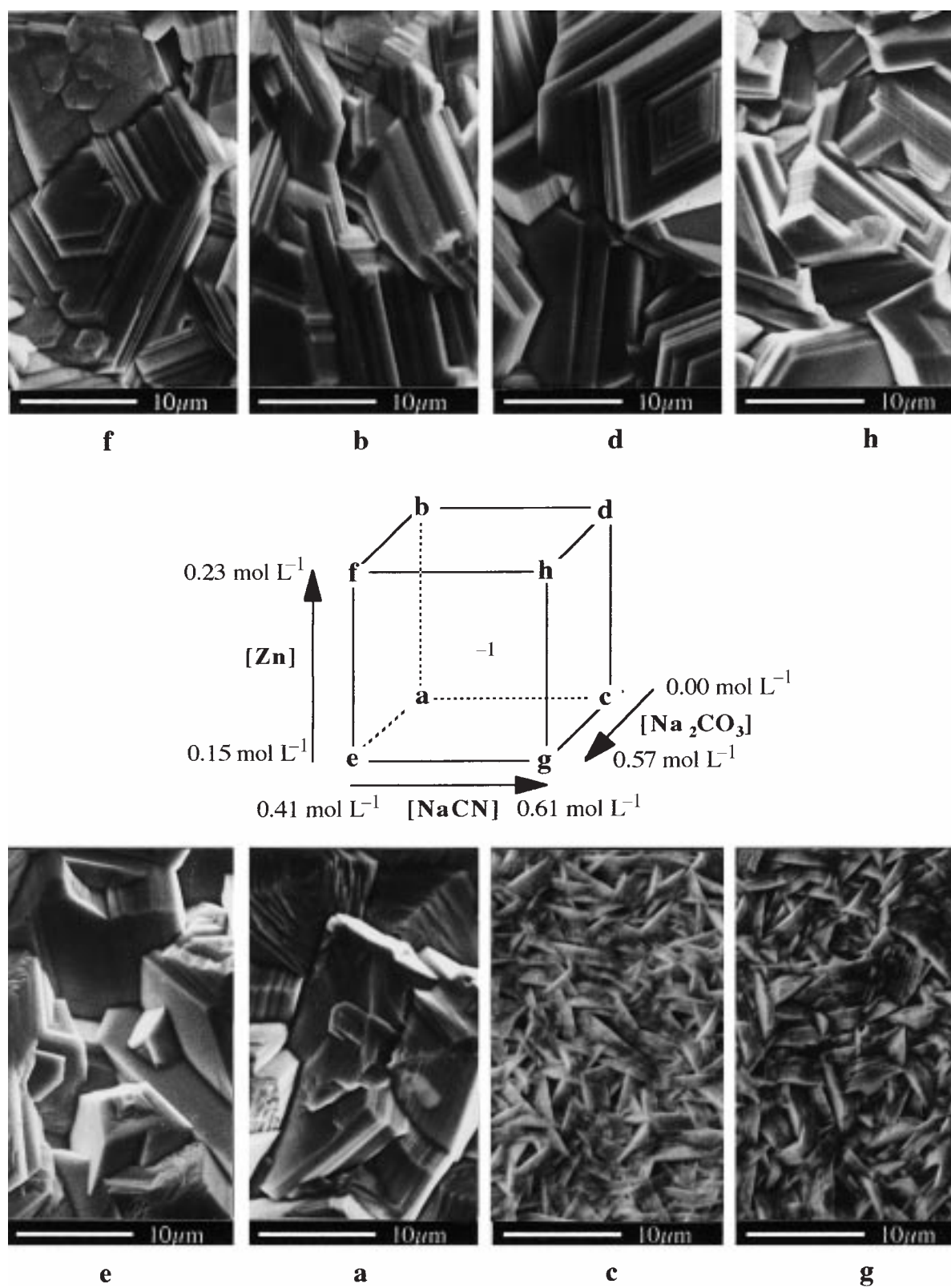


Fig. 4. SEM micrographs of deposits from various low cyanide zinc electrolytes under potentiostatic control ($i = 10 \text{ mA cm}^{-2}$ after electrolysis with 25.2 C cm^{-2}).

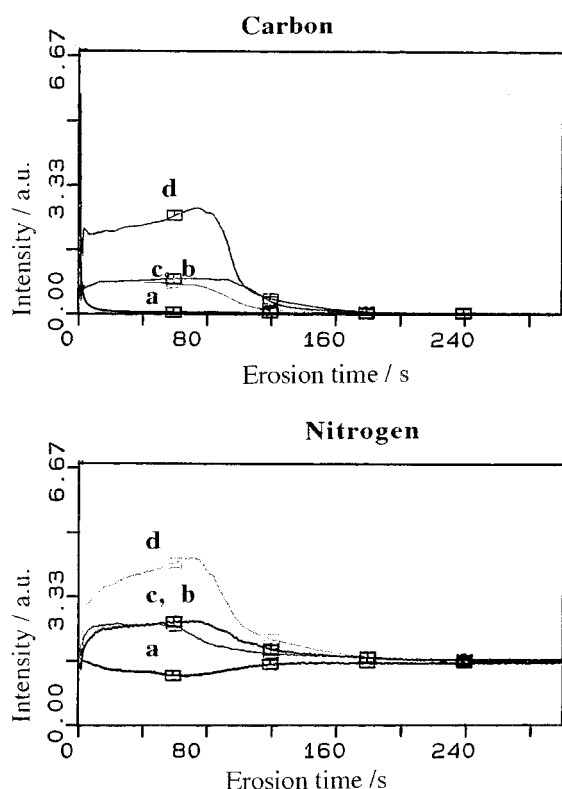


Fig. 5. GDOS concentration profile of carbon and nitrogen obtained on zinc deposits from electrolytes (a) without additive, (b) with 1 ml L⁻¹ of brightening agent (c) with 2 ml L⁻¹ of brightening agent, (d) with 5 ml L⁻¹ of brightening agent.

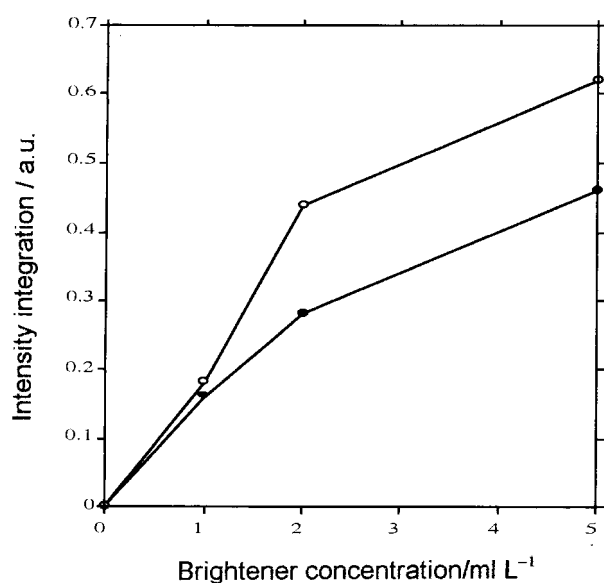


Fig. 6. Plot of concentrations of carbon (●) and nitrogen (○) in zinc deposits against brightener concentration in the zinc plating electrolyte.

together, is therefore $I = 1235 = 1246 = 3456$. This defining relation is the key to determining all the relationships that exist between the confounding pattern.

Cathodic efficiency and the variation in thickness are quantified. Ignoring interactions among three or more factors, and using the complete generating relations, the sixteen effects of the test variables on cathodic efficiency η are given in Table 5. Only workload volume (V), current density (I), perforation size (P) and part size (S), have important effects on the response. Cathodic efficiency does not depend on rotational speed (R) and electrical charge (Q). Therefore, the seven sets of two-factor interactions confounded in groups of two or three are simplified, and only two factor interactions associated with these four parameters are underlined:

$$\eta = 85.1 - 2.6 \times V - 3.9 \times I + 2.4 \times P + 2.9 \times S + 1.7 \times \underline{IS} + 1.3 \times \underline{VP} - 1.5 \times \underline{VI} + 1.3 \times \underline{VS} - 1.0 \times \underline{PS}$$

The effects of increasing barrel load and the current density associated with the interaction cause a subsequent decrease in efficiency. This phenomenon can be explained by an increased depletion of zinc in the vicinity of the workload, causing a drop in the zinc/cyanide ratio and by the local increase in the cyanide ion concentration, which tends to diminish the dissociation of complexed metal ions. The effects of perforation size and part size show a positive slope. It appears that the larger the holes, the greater the cathode efficiency. The perforation effect may be explained by an increase in the exchange of the metal-depleted solution from inside to outside the barrel. There is a direct relationship between the size of parts and the volume of the load in the barrel. If the parts are small, the density of the workload is high and parts cannot tumble freely in the barrel. This may lead to decreased efficiencies and inconsistency from part to part.

Barrel rotation speed and electrical charge do not significantly affect cathode efficiency for the range examined. Thus, it is reasonable to speculate that the composition equilibrium resulting from the mass exchange from inside to outside the rotating barrel is rapidly obtained. However, if this state induces a difference in composition that is a function of exchange speed, increasing barrel perforations and apparent density of the load, should increase cathode efficiency.

3.2.2. Metal thickness variation

There are two distinct types of variation in deposit thickness. Variation in local thickness for a single part, and variation in individual average thickness between one part and another. However, variation in local

Table 4. Factorial experimental design 2^{6-2} with the generators $\mathbf{I} = 1235 = 1246 = 3456$

Test	1+...	2+...	12+ 35+ 46+...	3+	13+ 25+...	23+ 15+...	5+...	4+...	14+ 26+...	24+ 16+...	6+...	34+ 56+...	134+...	234+...	45+ 36+...	I+...
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1
3	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	1
4	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1
5	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1
6	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1
7	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	1	1	1
8	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1	1	-1	-1	1
9	-1	1	-1	1	-1	1	-1	1	-1	-1	-1	1	-1	1	-1	1
10	-1	1	-1	1	-1	1	-1	-1	1	1	1	-1	1	-1	1	1
11	-1	1	-1	-1	1	-1	1	1	-1	-1	-1	-1	1	-1	1	1
12	-1	1	-1	-1	1	-1	1	-1	1	1	1	1	-1	1	-1	1
13	-1	-1	1	1	-1	-1	1	1	-1	1	1	1	-1	-1	1	1
14	-1	-1	1	1	-1	-1	1	-1	1	-1	-1	-1	1	1	-1	1
15	-1	-1	1	-1	1	1	-1	1	-1	1	1	-1	1	1	-1	1
16	-1	-1	1	-1	1	1	-1	-1	1	-1	-1	1	-1	-1	1	1

Table 5. Levels for the plating conditions parameters

	Factor 1 V Workload volume /%	Factor 2 R Rotation speed /rpm	Factor 3 Q Electric charge /C dm ⁻²	Factor 4 I Current density /A dm ⁻²	Factor 5 P Perforation size /mm ²	Factor 6 S Pieces size
Low level -1	25	5	1500	0.5	0.03	small
High level +1	50	10	3000	1.0	0.50	big

thickness for a single part is a serious plating problem, since in most specifications it is not local thickness but minimum individual average thickness that is an operational requirement. The variation in thickness between one part and another is therefore important to platers. This aspect of plating has been discussed by many workers [8–10] who have tried to determine the effect of distribution of variations in barrel design, character of component, and thickness of deposit. Equipment factors such as rotation speed, or plating conditions such as current density, were not examined. Therefore, we will study the physical factors that strongly influence thickness variation. The array configuration is the same as before (Table 6); Table 7 depicts results. It can be seen that there is no apparent connection between metal variation and cathode efficiency. Thickness does not significantly vary for the range of current density, speed of rotation and perforation size ranges examined. The electrical charge and part size show negative slopes of, respectively, -0.9 and -1.4 , while the main effect of workload volume is positive ($+1.1$). The effect of these three parameters must therefore be assessed jointly rather than individually. The interaction effect must also be examined. It appears that the higher the workload,

the lower the electrical charge, and the lower the higher the variation. These effects are not surprising and are principally due to the loss of electrical continuity.

4. Conclusion

This study aimed at analysing how the composition and physical factors of a principal low cyanide solution influence the processing of a zinc deposit. The first part demonstrated that an experimental design can be implemented to determine the effects of electrolyte components on cathodic efficiency and deposit morphology during zinc electroplating. By using mathematical relationships, interactions between variables that would go unnoticed in one-at-a-time experimentation can be discovered. Brightening agent, sodium cyanide concentration and zinc metal content strongly influence cathodic efficiency. The morphologies of deposits vary with the change in concentrations of the solution components.

The additive has an inhibiting action on growth and favors bidimensional germination. Without additives, deposits are fine-grained with a decrease in efficiency. By

Table 6. Results and effects of the plating conditions upon the cathodic efficiency η

Test	η_1 /%	η_2 /%	η_{average} /%	Response notation		Effects	Significant?*
1	86.7	86.6	86.7	Mean ₊₊₊	I ₊₊₊	85.1	
2	90.7	90.5	90.6	V ₊₊₊	1 ₊₊₊	-2.6	yes
3	80.0	79.6	79.8	R ₊₊₊	2 ₊₊₊	0.2	no
4	80.5	80.3	80.4	Q ₊₊₊	3 ₊₊₊	0.3	no
5	66.5	66.6	66.5	I ₊₊₊	4 ₊₊₊	-3.9	yes
6	88.4	88.8	88.6	P ₊₊₊	5 ₊₊₊	2.4	yes
7	75.5	75.5	75.5	S ₊₊₊	6 ₊₊₊	2.9	yes
8	92.0	91.9	92.0	VR + QI + PS	12 + 35 + 46	1.7	yes
9	79.9	79.8	79.8	VQ + RP ₊₊₊	13 + 25 ₊₊₊	0.3	no
10	90.5	90.2	90.4	RQ + VP ₊₊₊	23 + 15 ₊₊₊	1.3	yes
11	84.4	84.4	84.4	VI + RS ₊₊₊	14 + 26 ₊₊₊	-1.5	yes
12	89.8	90.2	90.0	RI + VS ₊₊₊	24 + 16 ₊₊₊	1.3	yes
13	89.5	89.2	89.4	QI + PS ₊₊₊	34 + 56 ₊₊₊	-1.0	yes
14	91.5	91.8	91.6	VQI ₊₊₊	134 + ₊₊₊	-0.2	no
15	87.4	87.9	87.6	RQI ₊₊₊	234 + ₊₊₊	-0.1	no
16	88.5	88.3	88.4	QS + IP ₊₊₊	36 + 45 ₊₊₊	0.3	no

* After analysis of variables (ANOVA)

Table 7. Results and effects of the plating conditions parameters upon the coefficient of variation C_v

Test	C_{v1} /%	C_{v2} /%	$C_{v(\text{average})}$ /%	Response notation		Effects	Significant?*
1	5.7	5.9	5.8	Mean ₊₊₊	I ₊₊₊	7.7	
2	7.9	8.2	8.1	V ₊₊₊	1 ₊₊₊	1.1	yes
3	8.3	8.6	8.5	R ₊₊₊	2 ₊₊₊	-0.0	no
4	11.9	11.5	11.7	Q ₊₊₊	3 ₊₊₊	-0.9	yes
5	11.7	11.9	11.8	I ₊₊₊	4 ₊₊₊	0.4	no
6	6.4	6.5	6.5	P ₊₊₊	5 ₊₊₊	-0.2	no
7	12.0	11.1	11.6	S ₊₊₊	6 ₊₊₊	-1.4	yes
8	6.7	6.4	6.5	VR + QI + PS	12 + 35 + 46	-0.3	no
9	6.5	6.3	6.4	VQ + RP ₊₊₊	13 + 25 ₊₊₊	0.2	no
10	4.6	4.6	4.6	RQ + VP ₊₊₊	23 + 15 ₊₊₊	-0.6	no†
11	9.6	9.6	9.6	VI + RS ₊₊₊	14 + 26 ₊₊₊	0.2	no
12	6.9	7.1	7.0	RI + VS ₊₊₊	24 + 16 ₊₊₊	-0.6	yes
13	4.9	4.7	4.8	QI + PS ₊₊₊	34 + 56 ₊₊₊	-0.1	no
14	6.6	6.7	6.6	VQI ₊₊₊	134 ₊₊₊	0.2	no
15	6.8	6.9	6.8	RQI ₊₊₊	234 ₊₊₊	0.1	no
16	7.6	7.4	7.5	QS + IP ₊₊₊	36 + 45 ₊₊₊	0.0	no

* After analysis of variables (ANOVA)

† An additional run has been carried out to determine whose of these two interactions are responsible for the observed results. The new estimates are: $RQ = -0.4$ and $VP = -0.2$

adjusting the solution, it is possible to control cathodic efficiency and to some extent the structure of deposits and thereby their properties.

The second part of the study shows how physical factors such as equipment and plating conditions affect cathodic efficiency and scatter. Equipment and plating conditions are as important as the solution for cathodic efficiency. Cathodic efficiency is not affected by rotation speed and electrical charge but does depend on how full the barrel is, current density, perforation size and part size. The variation in thickness, on the other hand, increases as the workload volume increases. It is also

affected by the electrical charge and part size, but does not depend on rotational speed, current density and perforation size. The physical factors that improve current efficiency do not improve thickness variation.

Acknowledgements

The authors thank the Rivex Company for its financial support. We also thank the Microscopy Centre of Besançon for providing the SEM facilities and to Professor Douglade, University of Reims, for the X-ray analysis.

References

1. J.C. Catonné, *Actualité chimique* **1** (1992) 67.
2. A.W. Wallbank, *Proc. Amer. Electroplaters' Soc.* **46** (1959) 306.
3. P. Glab, R. Scott Modjeska and S.P. Gary, *Proc. Amer. Electroplaters' Soc.* **47** (1960) 184.
4. H. Henig, *Galvanotechnik-Oberflächenschutz* **1** (1966) 1.
5. L. Nanis, *Plating* **58** (1971) 805.
6. S.E. Craig, R.E. Harr and P. Mathiesen, *Plating* **61** (1974) 1101.
7. H.D. Hedrich, W. Günter and Ch.J. Raub, *Surf. Technol.* **11** (1980) 443.
8. W.C. Geissman and R.A. Carlson, *Proc. Amer. Electroplaters' Soc.* **39** (1952) 153.
9. F.I. Nobel, B.D. Ostrow, R.B. Kessler and D.W. Thomson, *Plating* **53** (1966) 1099.
10. F.I. Nobel and D.W. Thomson, *Plating* **57** (1970) 469.
11. M.J. Burrill and C.M. Prosser, *Trans. I.M.F.* **52** (1974) 43.
12. D.R. Gabe and H.K. Tse, *Trans. I.M.F.* **58** (1980) 4.
13. J.A. Zehnder and al, *Plat. Surf. Finish.* **9** (1975) 862.
14. H.D. Hedrich, *Metalloberfläche* **34** (1980) 462.
15. W. Paatsch, *Metalloberfläche* **32** (1978) 12.
16. S.P. Bagaev and K.S. Pedan, *Prot. Met.* **20** (1984) 883.
17. J. McBreen, *Electrochem. Soc. Proc.* **92** (1992) 248.
18. M.G. Vigier, 'Pratique des plans d'expérience' (Ed. Organisation, Paris, 1988).
19. S.N. Deming and S.L. Morgan, 'Experimental Design, Data Handling in Science and Technology', vol 11 (Elsevier, Amsterdam, 1993).
20. M. Wery, Thèses, Université Besançon (1995).
21. H. Geduld, 'Zinc Plating' (Finishing Publications Ltd, Teddington, 1988).
22. R. Tournier, 'Fiches techniques' (Libr. des Traitements de Surface, Paris, 1993).